pentaneethylaminium radical where the linearity of hydrogen transfer is the dominant factor.[7]

Experimental Section

N-Ethylcyclohexanecarboxamide.—To a cold solution of 5.0 g (0.034 mole) of cyclohexanecarbonyl chloride[13] in 20 ml of dry benzene was added with cooling a cold solution of 3.52 g (0.080 mole) of ethylamine in 20 ml of dry benzene. After standing for 12 hr at ice-bath temperature, the reaction mixture was washed with 1 *N* sodium hydroxide, water, and then with dilute hydrochloric acid. The aqueous washings were made basic, combined, and extracted with benzene. The benzene solutions were combined and dried; the solvent was removed to yield 5.18 g (98%) of the desired amide as white crystals, mp 98.0–99.5° (lit.[14,15] mp 95, 92°).

N-Ethylcyclohexanemethylamine.—A solution of 5.0 g (0.032 mole) of N-ethylcyclohexanecarboxamide in 100 ml of anhydrous ether was added dropwise to a stirred slurry of 5.0 g (0.132 mole) of lithium aluminum hydride in 25 ml of anhydrous ether. The reaction mixture was stirred for 8 hr and 20 ml of water was added dropwise with cooling. The reaction mixture was stirred for 0.5 hr and the inorganic salts were removed by filtration and washed thoroughly with ether. The ethereal solution was dried over anhydrous magnesium sulfate and the drying agent was removed by filtration. Removal of the solvent and fractional distillation of the residue gave 3.38 g (74%) of N-ethylcyclohexanemethylamine: bp 69–70° (13 mm), $n^{31}\mathrm{D}$ 1.4480.

6-Ethyl-6-azabicyclo[3.2.1]octane (2) *via* the Hofmann–Löffler–Freytag Reaction of N-Chloro-N-ethylcyclohexanemethylamine.—A solution of 26 g (0.185 mole) of N-ethylcyclohexanemethylamine and 26 g (0.196 mole) of N-chlorosuccinimide in 500 ml of ether was stirred for 3 hr. The succinimide which formed was precipitated by the addition of 500 ml of petroleum ether (bp 30–60°). The succinimide was removed by filtration and the filtrate concentrated on a rotary evaporator.

The residue was dissolved with cooling in 200 ml of cold 85% sulfuric acid contained in a quartz vessel. The reaction mixture was flushed with nitrogen, stoppered, and irradiated with a bank of ten 15-w Sylvania Blacklite fluorescent tubes for 55 hr at 10°. The reaction mixture was made basic with cold 40% sodium hydroxide (external cooling required) and the resultant basic solution was steam distilled until the distillate was no longer basic to pH paper. The receiver from the steam distillation contained enough dilute hydrochloric acid to neutralize the distilling amine. This acid solution was concentrated to *ca.* 300 ml on a rotary evaporator, made basic, and continuously extracted with ether for 72 hr. The ether extract was dried over anhydrous magnesium sulfate, the drying agent removed by filtration, and the solvent distilled off to leave an amber liquid containing a mixture of secondary and tertiary amines.

The mixture of amines was reacted with 200 ml of 20% sodium hydroxide and excess benzenesulfonyl chloride. After stirring for 12 hr, the solids which formed were removed by filtration and the filtrate was continuously extracted with ether for 72 hr. The extract was dried over anhydrous magnesium sulfate. Removal of the drying agent and solvent followed by distillation of the residue gave 2.53 g (10%) of **2** which was shown to be 95% pure by vpc on 15% Ucon 50-HB5100 on 42–60 firebrick. Preparative vpc provided analytically pure material.

Anal. Calcd for $C_9H_{17}N$: C, 77.63; H, 12.31; N, 10.06. Found: C, 77.75; H, 12.23; N, 10.08.

6-Azabicyclo[3.2.1]octan-7-one (4).—*m*-Aminobenzoic acid was converted into **4** in a two-step process consisting of catalytic hydrogenation and thermal cyclization according to the procedure of Hewgill and Jeffries.[8] Substitution of 5% ruthenium on carbon for the Adams catalyst used by these earlier workers raised the yield in the catalytic hydrogenation from 21 to 85% of *cis*-3-aminocyclohexanecarboxylic acid. Thermal cyclization afforded **4** in 70% yield.

6-Ethyl-6-azabicyclo[3.2.1]octan-7-one (5).—A mixture of 0.39 g (0.01 mole) of sodium amide and 0.759 g (6.06 mmoles) of **4** in 10 ml of toluene was refluxed for 4 hr, cooled, and excess ethyl bromide was added. The reaction mixture was refluxed for 13 hr, cooled; the precipitated salts were removed by filtration. The solvent was removed *via* fractional distillation and the residue was vacuum distilled to give 0.42 g (45%) of **5**, bp 76° (0.45 mm). Preparative vpc on 5% SE 30 on 60–80 Chromosorb W gave an analytical sample, $n^{25}\mathrm{D}$ 1.4855.

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.31; H, 9.81; N, 9.28.

6-Ethyl-6-azabicyclo[3.2.1]octane (2).—Following the procedure outlined above, 2.24 g of **4** was ethylated and immediately reduced with lithium aluminum hydride (2.0 g) in 200 ml of anhydrous ether over a 10-hr period. Water (8.0 g) was added dropwise to the cooled reaction mixture and the precipitated inorganic salts were removed by filtration. The filtrate was dried over anhydrous magnesium sulfate and filtered; the solvent was distilled off. The residue was fractionally distilled to yield 1.05 g of **2** (42% yield from **4**), bp 75–76° (29 mm). The infrared and nuclear magnetic resonance spectra were identical with those of the product obtained from the Hofmann–Löffler–Freytag reaction of **1**.

Registry No.—2, 14002-06-3; 5, 14002-07-4; N-ethylcyclohexanemethylamine, 14002-08-5.

Acknowledgment.—The authors are indebted to the National Cancer Institute for Public Health Service Grant CA-07110 which supported this investigation.

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[13] Purchased from Aldrich Chemical Co. and used without further purification.

[14] J. v. Braun, F. Jostes, and W. Munch, *Ann.*, **453**, 113 (1927).

[15] E. K. Harvill, R. M. Herbst, E. C. Schreiner, and C. W. Roberts, *J. Org. Chem.*, **15**, 662 (1950).

Liquid Phase Oxidations of Cyclic Alkenes. II[1]

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A previous paper of the same title[2a] described the effect of ring size on the competition between the addition and hydrogen abstraction mechanisms in oxidations of cyclic alkenes. This note presents some additional results obtained with norbornene and cyclododecatriene which were not appropriate for inclusion in our more recent papers[2b,c] on oxidations of acylic alkenes.

Oxidation of Norbornene[2.2.1]bicycloheptene.—The oxidation of this hydrocarbon (from Aldrich Chemical Co.) is of interest because the allylic hydrogen atoms are at bridgehead positions and the double bond is "strained"; that is, the C_1–C_2–C_3 angle is less than the 120° preferred by normal olefins.[3]

Details are given in Table I. The initial rate of oxygen absorption, 0.0253 mole/l. hr, was followed by moderate autocatalysis, and gives a calculated $k_p/(2k_t)^{1/2}$ value of 0.268 (l./mole hr)$^{1/2}$. Thus the reactivity of norbornene in oxidation is nearly equal to that of cyclohexene (0.31).

A titration of the reaction mixture showed that only 5% of the absorbed oxygen appeared as hydroperoxide. The oxidate was analyzed by the usual proce-

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[1] Research sponsored by AFOSR (SRC)-OAR, U.S.A.F. Contract No. AF49(638)-1102.

[2] (a) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4824 (1965); (b) D. E. Van Sickle, F. R. Mayo, R. M. Arluck, and M. G. Syz, *ibid.*, **89**, 967 (1967); (c) D. E. Van Sickle, F. R. Mayo, E. S. Gould, and R. M. Arluck, *ibid.*, **89**, 977 (1967).

[3] The heat of hydrogenation is 25.7 kcal/mole for cyclopentene and 33.1 kcal/mole for norbornene; R. B. Turner, W. R. Meadow, and R. E. Winkler, *ibid.*, **79**, 4116, 4133 (1957).

TABLE I

OXIDATION OF NORBORNENE AT 60°[a]

Product	Mmoles	Mmoles of C_7H_{10}	Mmoles of O_2
Norcamphor + norbornene oxide	1.37	1.37	0.68
Norbornanediol	0.53	0.53	0.53
Unidentified volatiles (3)	0.17	0.17	0.17
CO_2	0.44	...	0.44
Residue[b]	7.32	7.32	8.62
		9.39	10.44

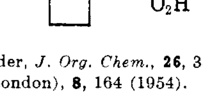
[a] C_7H_{10} (244.8 mmoles) in 20.57 g of benzene, [ABN] = 0.00956 *M*, $[C_7H_{10}]_{60}$ = 4.68 *M*, absorbed 13.8 mmoles of O_2 in 289 min at an average oxygen pressure of 47 psia. The aliquot taken for analysis corresponds to 11.2 mmoles of O_2. [b] Material (971 mg) that analyzed as $C_7H_{10.7}O_{2.34}$ and contained 0.674 mmole of titratable hydroperoxide.

dure of removing the benzene and unreacted norbornene by vacuum distillation; remaining products were separated into volatile and nonvolatile fractions. The volatile fraction was found to contain no hydroperoxide and was analyzed directly by glpc. The residue was analyzed for carbon and hydrogen, with the results shown in Table I.

Clearly the major product of norbornene oxidation is the nonvolatile residue. We suspect that, in addition to some norbornene–oxygen copolymer, derivatives of cyclopentane-1,3-dicarboxaldehyde are present. The subsequent oxidation of this material to peracid accounts for the small peroxide titer and for the oxygen content in excess of the theoretical for the copolymer. We attribute the high hydrogen content of the residue to analytical error. The product analyses in Table I show that none of the norbornene oxidizes by the abstraction mechanism and that no norbornene-1-hydroperoxide is formed. The high reactivity of the olefin toward alkylperoxy radicals must therefore reside in the double bond. Bridging of the cyclohexene ring has thoroughly deactivated the allylic bridgehead hydrogen atoms and increased the reactivity of the double bond by eight- to ninefold.

1,5,9-Cyclododecatriene.—The oxidation of this 1,5-diene was studied briefly in a search for transannular effects like those observed in strong acid treatment.[4] Two experiments were carried out with the undiluted hydrocarbon obtained from Columbia Carbon Co. At 60°, with 257 mmoles of $C_{12}H_{18}$, 0.00963 *M* ABN, and 50–60-psia oxygen, 15.6 mmole oxygen was absorbed in 631 min. The initial rate was 0.0211 mole/l. hr, with a chain length of 51. At 70° with 0.00963 *M* ABN and 50-psia oxygen, the rate was 0.0622 mole/l. hr with a chain length of 37. These rates are one-half to one-third of that found with cyclohexene and about twice that found with cyclododecene. In both experiments strong autocatalysis was observed and iodometric titration indicated that only 52.5% (60° run) of the absorbed oxygen was present as hydroperoxide, a common situation with 1,5-dienes where nontitrable cyclic peroxides are formed.[5] The product is therefore taken to be mainly corresponding to abstractions of allylic hydrogen atoms and intramolecular additions of the resulting peroxy radicals.

$C_{12}H_{18}O_4$,



Removal of the unreacted hydrocarbon from the 70° run followed by exhaustive hydrogenation of the residue gave a mixture of alcohols. Acetylation of the alcohols followed by chromatography indicated five components present, all of approximately equal volatility. Although the exhaustive hydrogenation consumed only 2.73 moles of hydrogen per mole of residue, it is not evident that much transannular ring closure occurred. Conversion of the alcohol mixture to hydrocarbon skeleton by the procedure of Cope and coworkers[6] gave a mixture which is 85–90% cyclododecane. A preliminary shoulder on the main peak of the gas chromatography trace could[7] be bicyclo[4.6.0]-dodecane, but would constitute only 10–15% of the mixture. Thus, little or no transannular carbon–carbon-bond formation occurred at an average oxygen pressure of 50 psia.

Registry No.—Norbornene[2.2.1]bicycloheptene, 498-66-8; 1,5,9-cyclododecatriene, 4904-61-4.

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[4] E. T. Niles and H. R. Snyder, *J. Org. Chem.*, **26**, 330 (1961).

[5] L. Bateman, *Quart. Rev.* (London), **8**, 164 (1954).

[6] A. C. Cope, *et al.*, *J. Am. Chem. Soc.*, **84**, 2170 (1962).

[7] An alternate possibility is *n*-dodecane (which arises by reduction of products from oxidative cleavage of one olefin bond of the triene).

Reaction of 2-Carbethoxycycloalkanones with 1,4-Dichloro-2-butene

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In an investigation of methods of preparation of bicyclo[4.3.1]dec-3-en-10-one (Ic), it was observed that sodium ethoxide produces cleavage of 2-carbethoxycyclohexanone while sodium *t*-amylate catalyzes alkylation.[1]

When sodium *t*-amylate was used as the base in the alkylation of 2-carbethoxycycloalkanones of five-, six-, and seven-membered rings with 1,4-dichloro-2-butene, only 2-carbethoxycyclohexanone gave a bicyclic compound, Ia. 2-Carbethoxycyclopentanone and 2-carbethoxycycloheptanone both gave almost entirely polymeric material. Simple alkylation of all three compounds by 1-chloro-4-ethoxy-2-butene was accomplished in the presence of sodium *t*-amylate. When sodium ethoxide was used as the base in the reaction with either 1,4-dichloro-2-butene or 1-chloro-4-ethoxy-2-butene, 2-carbethoxycyclopentanone and 2-carbethoxycyclohexanone[2] both were cleaved and 2-carbethoxycycloheptanone again was alkylated without cleavage.

The structure of the cleavage product in the reaction with 2-carbethoxycyclohexanone, ethyl 6-carbethoxy-10-ethoxy-8-decenoate (II), was indicated by the infrared spectrum, which showed characteristic absorption at 5.75 and 8.50 μ and failed to indicate a carbonyl

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(1) Spiro[4.5]dec-2-en-6-one instead of bicyclo[4.3.1]dec-3-en-10-one was formed by the *t*-amylate-catalyzed reaction between cyclohexanone and 1,4-dichloro-2-butene.

(2) Isolation of some 2-carbethoxy-2-(4-ethoxy-2-butene-1-yl)cyclohexanone (III) showed that cleavage of 2-carbethoxycyclohexanone was accompanied by some alkylation without cleavage.